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XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.TRIANILIDODINITROBENZOL AND CERTAIN
RELATED COMPOUNDS.

BY C. LORING JACKSON AND H. N. HERMAN.

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In a paper * published last year by one of us and W. B. Bentley, two forms of anilidotrinitrophenyltartronic ester were described, one of which was red and melted at 143° , the other yellow with a melting point of 122° . We have undertaken a more complete study of this subject because the existence of these two modifications, if they are really chemical isomeres, is not explained by any of the present theories of isomerism, unless indeed this should prove to be a case of an unsymmetrical nitrogen atom according to the hypothesis proposed by Hantzsch and Werner.† The anilidotrinitrophenyltartronic ester can be prepared in quantity only at a great expense of time and labor. It seemed wise, therefore, to begin our work by an examination of some related substances for similar modifications, as, if such were discovered in the case of a more accessible compound, their complete characterization could be worked out with greater ease. Unfortunately, as the new modifications obtained during these experiments were not so well marked as those already found, they could not be used to advantage for this purpose, and this work has taken so much time that the fuller study of the two forms of anilidotrinitrophenyltartronic ester could not be entered upon before the departure of one of us from Cambridge. The work contained in this paper, therefore, relates principally to the trianilidodinitrobenzol, which we have found appears in both red and yellow crystals, differing most strikingly in color and habit, but melting apparently at the same temperature, and passing from one

* These Proceedings, Vol. XXVI. p. 67.

† Ber. d. ch. G., 1890, p. 11.

form to the other with great ease, so that it is doubtful whether they should be considered true isomeres. Nevertheless, it has seemed to us that, in the present state of our knowledge of isomeres, a description of such closely related modifications as these might be of advantage to the science, and we therefore publish our results, which we think the more interesting because the triparatoluidodinitrobenzol shows an exactly similar behavior. On the other hand, we have not succeeded as yet in obtaining such forms from the triorthotoluidodinitrobenzol, although it is possible that they may exist, but that the second modification is less stable than those of the anilido and paratoluido compounds.

In searching for isomeric forms of the trianilidodinitrobenzol, which we have done by a great number of varied experiments, we discovered a compound of this substance with chloroform having the formula $C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3$, which crystallized in blackish red well formed prisms, but lost its chloroform partially even at ordinary temperatures. A similar addition product was obtained with the corresponding para- but not with the orthotoluido compound; an attempt will be made in this Laboratory to trace the limits of this reaction.

Numerous attempts to prepare a second modification of trianilidotrinitrobenzol or of anilidotrinitrophenylmalonic ester have led to negative results without exception, as no change in the full yellow color or the crystalline form of either of these substances could be observed, but this result seems so strange in view of the occurrence of two modifications of the trianilidodinitrobenzol on the one hand, and of the anilidotrinitrophenyltartonic ester on the other, that a more careful study of these substances will be made hereafter, and the work extended to other substances, in the hope of collecting in time enough observations to determine the cause of the isomerism of the substituted tartronic ester.

Experiments with Trianilidodinitrobenzol.

In searching for isomeric forms of the trianilidodinitrobenzol we studied more carefully than before the crystallization of it from various solvents, and found that, when a mixture of benzol and alcohol was used as the solvent, it appeared in crystals of two sorts, one the nearly square prisms of an orange color like that of potassic dichromate already described, the other as yellow as potassic chromate in bladed crystals, or plates looking like flattened monoclinic prisms terminated by two planes, or less commonly with square

ends, which, when the cooling took place rapidly, appeared in circular groups of little needles. These two modifications differed entirely in crystalline habit and color, and resembled strongly the yellow and red forms of anilidotrinitrophenyltartronic ester, the discovery of which had led us to undertake this work; but whereas the two esters showed a difference of 21° in their melting points (red 143° , yellow 122°), the yellow and red forms of the trianilido-dinitrobenzol melted at the same temperature, 179° . To be sure, the yellow form turned red at about 140° , but there were no signs of melting, and we do not feel that such a change from yellow to orange-red is definite enough to have much significance. The yellow form was also much less stable than the corresponding form of the anilidotrinitrophenyltartronic ester, so that we have not obtained it absolutely free from the orange modification. The best way for preparing it that we found was to crystallize the orange form from a mixture of benzol and alcohol containing much benzol, when a portion of the substance usually appeared in the yellow form. On the other hand, a single crystallization of the yellow crystals from a mixture of benzol and alcohol containing but little benzol was sufficient to convert them completely into the orange prisms. As it was possible that the yellow crystals might be a compound containing alcohol or benzol of crystallization, instead of an isomere, we heated to 100° 0.3190 gr. of the best we could obtain, which had been air dried, but found that the loss was only 0.0004 gr., showing that this is not the explanation of the occurrence of this form.

The presence of a small amount of impurity seemed to be favorable to the existence of the modification crystallizing in plates, as, if a little tribromdinitrobenzol was present, crystals were obtained of this form although usually a little more orange in color than that made from pure material, and these would undergo several crystallizations before they were converted into the orange form. A sample, which we obtained accidentally, was even more stable, and owed this stability to an oily impurity, the presence of which was indicated by the low melting point, and which we finally succeeded in separating, but only after a great number of crystallizations, when the substance passed into the orange form; the amount of this impurity, however, was very small, as shown by the following analyses:—

- I. 0.2522 gr. of the substance gave on combustion 0.6004 gr. of carbonic dioxide and 0.1086 gr. of water.

II. 0.2197 gr. of the substance gave 31.6 c.c. of nitrogen at a temperature of 25° and a pressure of 755.4 mm.

	Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2$	Found.	
		I.	II.
Carbon	65.31	64.94	
Hydrogen	4.30	4.79	
Nitrogen	15.88		15.95

The substance gave no test for bromine with a copper wire, or even when treated according to the method of Carius. As the amount of impurity is so small that we thought it could have no effect, we have used this preparation for the determination of the molecular weight of the yellow modification, which, with that of the orange prisms, was made by the method of Raoult, using benzol as the solvent, since preliminary experiments had shown that these compounds were not sufficiently soluble in glacial acetic acid.

Yellow Plates.

Substance 0.2290 gr. Benzol 10.299 gr. Depression 0°.27.

Orange Prisms.

Substance 0.2561 gr. Benzol 10.468 gr. Depression 0°.29.

From these results the following molecular weights are obtained:—

	Molecular Weight.
Yellow Plates	404
Orange Prisms	413
Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2$	441

There can be no doubt, therefore, that the substances are not polymeric. The benzol solutions obtained in the determinations were mixed with a little alcohol, and allowed to evaporate spontaneously, (the substance is deposited as a varnish from benzol alone,) when each yielded as the principal product the modification which had been originally dissolved in it, although in each case this was mixed with an insignificant amount of the other form.

From the observations given above we should infer that these two modifications of the trianilidodinitrobenzol are not true chemical isomeres, but physical isomeres, or perhaps rather that the substance is dimorphous.

We have made a great many experiments to get other isomeric forms of the trianilidodinitrobenzol, both by varying the method

of preparation in every way we could devise, and by treating the orange prisms with reagents, which usually convert one stereoisomeric form into another, but have met with no forms except the two already described.

Compound of Trianilidodinitrobenzol and Chloroform.

If in crystallizing the trianilidodinitrobenzol a mixture of chloroform and alcohol was used instead of benzol and alcohol, dark red well formed short prisms were obtained entirely different from either of the forms just described. The whole of the substance could be converted into these prisms, if the solution in chloroform and a little alcohol was allowed to evaporate at temperatures from 50° to 70°. This substance, however, proved to be, not an isomere, but a compound with chloroform, since on heating some of the dry crystals with sodic hydrate and aniline a strong odor of phenylisocyanide was perceived.

Our first attempts to analyze it showed that the chloroform was given up partially at ordinary temperatures, but that to drive off the remainder it was necessary to heat to 100°. Accordingly we proceeded as follows. A quantity of the orange trianilidodinitrobenzol melting at 179° was dissolved in warm chloroform, and after the addition of a little alcohol poured into a large watch-glass to crystallize; when nearly all the chloroform had evaporated, the crystals were pressed as quickly as possible between filter paper till free from adhering chloroform, and then transferred at once to a stoppered glass tube, in which they were weighed.

- I. 1.5012 gr. of the compound lost at 100° 0.3226 gr. of chloroform.
- II. 1.4455 gr. of the substance lost at 100° 0.3059 gr. of chloroform.

	Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3$.	I.	Found. II.
Chloroform	21.32	21.49	21.16

The residue was trianilidodinitrobenzol melting at 179°.

Properties of the Addition Compound of Trianilidodinitrobenzol and Chloroform. — This substance crystallizes in short thick prisms with both terminations well developed, apparently of the monoclinic system, which have a very dark brownish red color not unlike that of well crystallized potassic ferricyanide, and show a blue reflex. The chloroform is not securely held, part of it being given

up even at ordinary temperatures with great rapidity, whereas heating to 100° is necessary to drive out the last traces. On this account its presence has only a slight effect on the melting point, lowering it by a variable amount not exceeding 3° or 4° . Standing with alcohol if the crystals are small, or grinding them with it if they are large, also drives out the chloroform, leaving the usual orange prismatic form, and the same effect is produced by one crystallization from alcohol. Its action with other solvents was not studied.

Triparatoluidinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_2$. — 10 grams of tribromdinitrobenzol were heated with 18 grams of paratoluidine on the steam bath for eighteen or more hours; the reddish black product was freed from the excess of toluidine by standing with dilute hydrochloric acid, followed by careful washing with hot water, and then purified by crystallization from benzol and chloroform. The substance thus obtained was not, however, triparatoluidodinitrobenzol, but its addition compound with chloroform, as was shown by the isocyanide reaction, and the following analysis of the crystals dried by pressing between filter paper.

0.9079 gr. of the substance lost at 100° 0.1798 gr. of chloroform.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2CHCl_3$.	Found.
Chloroform	19.83	19.81

Properties of Addition Compound $C_6H(C_7H_7NH)_3(NO_2)_2CHCl_3$. — This substance crystallizes in long plates terminated at each end by two planes at a rather sharp angle to each other. It has a dark brownish red color and loses part of its chloroform even at ordinary temperatures, but does not seem to be decomposed by alcohol so easily as the corresponding anilido compound.

In order to obtain the triparatoluidodinitrobenzol the preceding compound was dried at 100° until all the chloroform had passed off, and then crystallized from alcohol with a little benzol until it showed the constant melting point 197° , when it was analyzed with the following results : —

- I. 0.1907 gr. of the substance gave on combustion 0.4707 gr. of carbonic dioxide and 0.1039 gr. of water.
- II. 0.2580 gr. of the substance gave on combustion 0.6351 gr. of carbonic dioxide and 0.1299 gr. of water.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found.	
		I.	II.
Carbon	67.09	67.30	67.14
Hydrogen	5.18	6.04	5.59

Properties of Triparatoluidodinitrobenzol. — This substance crystallizes from a mixture of benzol and alcohol in characteristic acute rhombic plates of a very dark purplish red color somewhat like that of well crystallized potassic ferricyanide, but redder and more purple. It melts at 197° , and is nearly insoluble in ethyl or methyl alcohol; freely soluble in benzol or chloroform; sparingly soluble in acetone or hot glacial acetic acid, almost insoluble in the latter solvent when cold.

If the dark brownish red plates of triparatoluidodinitrobenzol are boiled with alcohol, the alcoholic extract deposits on cooling thread-like felted crystals of a yellow color, which change to red in the neighborhood of 180° , and melt at 197° like the original rhombic plates. We have found it impossible, however, to convert the whole of the plates into the yellow felted needles by this process. To prove that the yellow crystals did not contain alcohol of crystallization a portion of the preparation was heated to 120° until constant, when it was found that the loss was not more than would be mechanically retained by such a very spongy substance. The dried substance was then analyzed with the following result: —

0.2096 gr. of the substance gave 26.9 c. c. of nitrogen at a temperature of $27^\circ.5$ and a pressure of 758.6 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found.
Nitrogen	14.49	14.10

We should add that 0.3991 gr. of the dark red plates air-dried when heated to 100° for four hours lost only 0.0004 gr., so that this substance also is free from alcohol or benzol of crystallization. These observations show that the triparatoluido compound appears in two forms similar to those discovered with the anilido compound. Some other solvents beside alcohol convert the red form partially into the yellow, notably ether and acetone.

Triorthotoluidodinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_2$.

This substance was most conveniently prepared by adding 12 gr. of tribromdinitrobenzol to 35 gr. of boiling orthotoluidine, stirring the mixture, and allowing it to cool as quickly as possible to

avoid the formation of purple dye stuff. The product was treated with dilute hydrochloric acid twice, allowing the mixture to stand for some time, and then washed thoroughly with water, after which it was purified by crystallization from benzol and alcohol, or chloroform and alcohol, until it showed the constant melting point 243° , when it was analyzed with the following result:—

0.2691 gr. of the substance gave 34 c. c. of nitrogen at a temperature of 23° and a pressure of 763.3 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$	Found.
Nitrogen	14.49	14.31

Properties.—The substance crystallizes in rather stout pointed needles of a full red color, which melt at 243° , and are somewhat soluble in hot ethyl or methyl alcohol, less soluble in either cold; freely soluble in chloroform, acetone, or hot benzol, not very soluble in cold benzol; slightly soluble in hot ligroine. Sodid hydrate had no apparent action on it. An attempt to make a chloroform compound from it led to no result, the substance crystallized from chloroform showing no loss when heated to 120° . Nor have we succeeded in finding a yellow modification, although we have tried the methods which yielded such modifications with the corresponding compounds of aniline and paratoluidine; we think further experiments of this sort necessary, however, before we can be certain that such a modification does not exist. The high melting point and the observations just mentioned indicate that this ortho compound is decidedly different from the corresponding para compound.